(54) Titre : CAOUTCHOUC NITRILE HYDROGENE DE FAIBLE POIDS MOLECULAIRE
(54) Title: LOW MOLECULAR WEIGHT HYDROGENATED NITRILE RUBBER

(57) Abrégé/Abstract:
A hydrogenated nitrite rubber having lower molecular weights and narrower molecular weight distributions than those known in the art can be prepared by the claim metathesis of nitrite butadiene rubber, followed by hydrogenation of the resulting metathesised NBR.

Abstract

A hydrogenated nitrile rubber having lower molecular weights and narrower molecular weight distributions than those known in the art can be prepared by the olefin
5   metathesis of nitrile butadiene rubber, followed by hydrogenation of the resulting metathesised NBR.

Low Molecular Weight Hydrogenated Nitrile Rubber

Field of the Invention.

The present invention relates to hydrogenated nitrile rubber polymers having

5   lower molecular weights and narrower molecular weight distributions than those known
in the art.

Background of the Invention

Hydrogenated nitrile rubber (HNBR), prepared by the selective hydrogenation of

10   acrylonitrile-butadiene rubber (nitrile rubber; NBR), is a specialty rubber which has very
good heat resistance, excellent ozone and chemical resistance, and excellent oil
resistance.   Coupled with the high level of mechanical properties of the rubber (in
particular the high resistance to abrasion) it is not surprising that HNBR has found
widespread use in the automotive (seals, hoses, bearing pads) oil (stators, well head

15   seals, valve plates), electrical (cable sheathing), mechanical engineering (wheels,
rollers) and shipbuilding (pipe seals, couplings) industries, amongst others.

Commercially available HNBR has a Mooney viscosity in the range of from about
55 to about 105, a molecular weight in the range of from about 200,000 to about

20   600,000, a polydispersity greater than 3.0 and a residual double bond (RDB) content in
the range of from about 1 to about 18% (by IR spectroscopy).

One limitation in processing HNBR is the relatively high Mooney Viscosity.   In
principle, HNBR having a lower molecular weight and lower Mooney viscosity would

25   have better processability.   Attempts have been made to reduce the molecular weight
of the polymer by mastication (mechanical breakdown) and by chemical means (for
example, using strong acid), but such methods have the disadvantages that they result
in the introduction of functional groups (such as carboxylic acid and ester groups) into
the polymer, and the altering of the microstructure of the polymer.   This results in

30   unacceptable changes in the properties of the polymer.   In addition, these types of
approaches, by their very nature, produce polymers having a broad molecular weight
distribution.

A hydrogenated nitrile rubber having a low Mooney (<55) and improved

35   processability, but which has the same microstructure as those rubbers which are

currently available, is difficult to manufacture using current technologies. The hydrogenation of NBR to produce HNBR results in an increase in the Mooney viscosity of the raw polymer. This Mooney Increase Ratio (MIR) is generally around 2, depending upon the polymer grade, hydrogenation level and nature of the feedstock.

5   Furthermore, limitations associated with the production of NBR itself dictate the low viscosity range for the HNBR feedstock. Currently, one of the lowest Mooney viscosity products available is Therban VP KA 8837 (available from Bayer), which has a Mooney viscosity of about 55 (ML 1+4 @ 100°C) and a RDB of about 18%.

10   Karl Ziegler's discovery of the high effectiveness of certain metal salts, in combination with main group alkylating agents, to promote olefin polymerization under mild conditions has had a significant impact on chemical research and production to date. It was discovered early on that some "Ziegler-type" catalysts not only promote the proposed coordination-insertion mechanism but also effect an entirely different

15   chemical process, that is the mutual exchange (or metathesis) reaction of alkenes ().

$$R^1\!\!=\!\!R^2 \quad + \quad R\!\!=\!\!R \quad \xrightarrow{\text{Catalyst}} \quad \underset{R}{\overset{R^1}{\|}} \; + \; \underset{R}{\overset{R^2}{\|}}$$

Figure 1

Acyclic diene metathesis (or ADMET) is catalyzed by a great variety of transition metal complexes as well as non-metallic systems. Heterogeneous catalyst systems based on metal oxides, sulfides or metal salts were originally used for the metathesis of

20   olefins. However, the limited stability (especially towards hetero-substituents) and the lack of selectivity resulting from the numerous active sites and side reactions are major drawbacks of the heterogeneous systems.

Homogeneous systems have also been devised and used to effect olefin

25   metathesis. These systems offer significant activity and control advantages over the heterogeneous catalyst systems. For example, certain Rhodium based complexes are effective catalysts for the metathesis of electron-rich olefins.

The discovery that certain metal-alkylidene complexes are capable of catalyzing the metathesis of olefins triggered the development of a new generation of well-defined, highly active, single-site catalysts. Amongst these, Bis-(tricyclohexylphosphine)-benzylidene ruthenium dichloride (commonly know as Grubb's catalyst) has been
5   widely used, due to its remarkable insensitivity to air and moisture and high tolerance towards various functional groups. Unlike the molybdenum-based metathesis catalysts, this ruthenium carbene catalyst is stable to acids, alcohols, aldehydes and quaternary amine salts and can be used in a variety of solvents (C_6H_6, CH_2Cl_2, THF, t-BuOH). The most commonly-used catalysts are based on Mo, W and Ru.

10

The use of transition-metal catalyzed alkene metathesis has since enjoyed increasing attention as a synthetic method. Research efforts have been mainly focused on the synthesis of small molecules, but the application of olefin metathesis to polymer synthesis has allowed the preparation of new polymeric material with unprecedented
15   properties (such as highly stereoregular poly-norbornadiene).

The utilization of olefin metathesis as a means to produce low molecular weight compounds from unsaturated elastomers has received growing interest. The principle for the molecular weight reduction of unsaturated polymers is shown in Figure 2. The
20   use of an appropriate catalyst allows the cross-metathesis of the unsaturation of the polymer with the co-olefin. The end result is the cleavage of the polymer chain at the unsaturation sites and the generation of polymer fragments having lower molecular weights. In addition, another effect of this process is the "homogenizing" of the polymer chain lengths, resulting in a reduction of the polydispersity. From an application and
25   processing stand point, a narrow molecular weight distribution of the raw polymer results in improved physical properties of the vulcanized rubber, whilst the lower molecular weight provides good processing behavior.
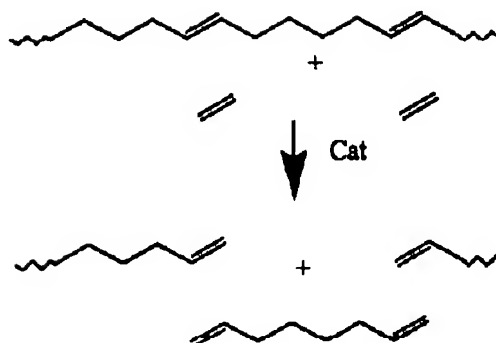
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Figure 2 Metathesis of Partially Unsaturated Polymer

The so-called "depolymerization" of copolymers of 1,3-butadiene with a variety of co-monomers (styrene, propene, divinylbenzene and ethylvinylbenzene, acrylonitrile,

5 vinyltrimethylsilane and divinyldimethylsilane) in the presence of classical Mo and W catalyst system has been investigated. Similarly, the degradation of a nitrile rubber using WCl6 and SnMe4 or PhC≡CH co-catalyst was reported in 1988. However, the focus of such research was to produce only low molecular fragments which could be characterized by conventional chemical means and contains no teaching with respect

10 to the preparation of low molecular weight nitrile rubber polymers. Furthermore, such processes are non-controlled and produce a wide range of products.

The catalytic depolymerization of 1,4-polybutadiene in the presence of substituted olefins or ethylene (as chain transfer agents) in the presence of well-defined

15 Grubb's or Schrock's catalysts is also possible. The use of Molybdenum or Tungsten compounds of the general structural formula {M(=NR₁)(OR₂)₂(=CHR); M = Mo, W} to produce low molecular weight polymers or oligomers from gelled polymers containing internal unsaturation along the polymer backbone was claimed in US 5,446,102. Again, however, the process disclosed is non-controlled, and there is no teaching with respect

20 to the preparation of low molecular weight nitrile rubber polymers.

Summary of the Invention

We have now discovered that hydrogenated nitrile rubber having lower molecular weights and narrower molecular weight distributions than those known in the art can be

prepared by the olefin metathesis of nitrile butadiene rubber, followed by hydrogenation of the resulting metathesised NBR.

Thus, one aspect of the disclosed invention is a saturated nitrile rubber having a
5 molecular weight (M_W) in the range of from about 30,000 to about 250,000, a Mooney viscosity (ML 1+4 100) of between about 3 and about 50, and a MWD (or polydispersity index) of less than about 2.5.

Description of the Invention

10 As used throughout this specification, the term "nitrile polymer" is intended to have a broad meaning and is meant to encompass a copolymer of a conjugated diene and an unsaturated nitrile.

The conjugated diene may be a C_4-C_6 conjugated diene. Non-limiting examples
15 of suitable such conjugated dienes may be selected from the group comprising butadiene, isoprene, piperylene, 2,3-dimethyl butadiene and mixtures thereof. The preferred C_4-C_6 conjugated diene may be selected from the group comprising butadiene, isoprene and mixtures thereof. The most preferred C_4-C_6 conjugated diene is butadiene.
20

The unsaturated nitrile may be a C_3-C_5 α,β-unsaturated nitrile. Non-limiting examples of suitable such C_3-C_5 α,β-unsaturated nitriles may be selected from the group comprising acrylonitrile, methacrylonitrile, ethacrylonitrile and mixtures thereof. The most preferred C_3-C_5 α,β-unsaturated nitrile is acrylonitrile.
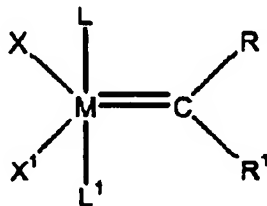25

Preferably, the copolymer comprises from about 40 to about 85 weight percent of the copolymer of bound conjugated diene and from about 15 to about 60 weight percent of the copolymer of bound unsaturated nitrile. More preferably, the copolymer comprises from about 60 to about 75 weight percent of the copolymer of bound
30 conjugated diene and from about 25 to about 40 weight percent of the copolymer of bound unsaturated nitrile. Most preferably, the copolymer comprises from about 60 to about 70 weight percent of the copolymer of bound conjugated diene and from about 30 to about 40 weight percent of the copolymer of bound unsaturated nitrile.

5

Optionally, the copolymer may further comprise a bound unsaturated carboxylic acid. Non-limiting examples of suitable such bound unsaturated carboxylic acids may be selected from the group comprising fumaric acid, maleic acid, acrylic acid, methacrylic acid and mixtures thereof. The bound unsaturated carboxylic acid may be present in an amount of from about 1 to about 10 weight percent of the copolymer, with this amount displacing a corresponding amount of the conjugated diolefin.

Further, a third monomer may be used in production of the nitrile polymer. Preferably, the third monomer is an unsaturated mono- or di-carboxylic acid or derivative thereof (e.g., esters, amides and the like).

Step 1: Metathesis

The metathesis reaction can be catalysed by compounds of formula I, II or III; as shown below :
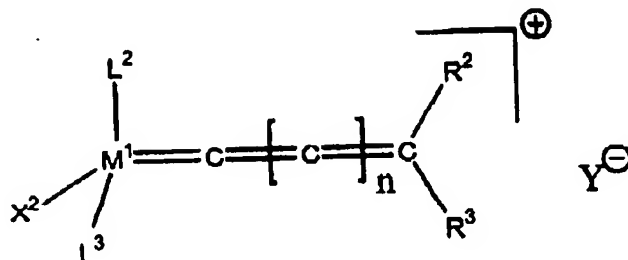

Formula I

wherein:

M is Os or Ru;

R and R^1 are, independently, hydrogen or a hydrocarbon selected from the group consisting of C_2-C_{20} alkenyl, C_2-C_{20} alkynyl, C_1-C_{20} alkyl, aryl, C_1-C_{20} carboxylate, C_1-C_{20} alkoxy, C_2-C_{20} alkenyloxy, C_2-C_{20} alkynyloxy, aryloxy, C_2-C_{20} alkoxycarbonyl, C_1-C_{20} alkylthio, C_1-C_{20} alkylsulfonyl and C_1-C_{20} alkylsulfinyl;

X and X^1 are independently selected anionic ligands; and

L and L^1 are, independently, ligands selected from the group consisting of phosphines, sulfonated phosphines, fluorinated phosphines, functionalized phosphines having up to three aminoalkyl-, ammoniumalkyl-, alkoxyalkyl-, alkoxylcarbonylalkyl-, hydrocycarbonylalkyl-, hydroxyalkyl- or ketoalkyl- groups, phosphites, phosphinites, phosphonites, phosphinamines, arsines, stibines, ethers, amines, amides, imines, sulfoxides, thioethers and pyridines; optionally, L and L^1 can be linked to one another to

from a bidentate neutral ligand wherein at least one of the above-mentioned functional groups is present.

Formula II

5 wherein:

M^1 is Os or Ru;

R^2 and R^3 are, independently, hydrogen or a hydrocarbon selected from the group consisting of C_2-C_{20} alkenyl, C_2-C_{20} alkynyl, C_1-C_{20} alkyl, aryl, C_1-C_{20} carboxylate, C_1-C_{20} alkoxy, C_2-C_{20} alkenyloxy, C_2-C_{20} alkynyloxy, aryloxy, C_2-C_{20} alkoxycarbonyl, C_1-C_{20}

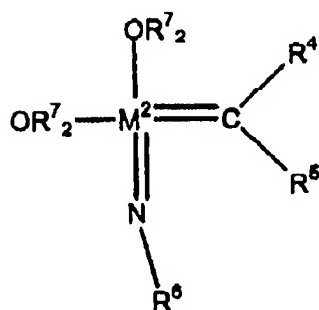10 alkylthio, C_1-C_{20} alkylsulfonyl and C_1-C_{20} alkylsulfinyl;

X^2 is selected from any anionic ligand; and

L^2 is a neutral π-bonded ligand, preferably but not limited to arene, substituted arene, heteroarene, independent of whether they are mono- or polycyclic;

L^3 is a ligand selected from the group consisting of phosphines, sulfonated

15 phosphines, fluorinated phosphines, functionalized phosphines bearing up to three aminoalkyl-, ammoniumalkyl-, alkoxyalkyl-, alkoxylcarbonylalkyl-, hydrocycarbonylalkyl-, hydroxyalkyl- or ketoalkyl- groups, phosphites, phosphinites, phosphonites, phosphinamines, arsines, stibenes, ethers, amines, amides, imines, sulfoxides, thioethers and pyridines;

20 Y^- is a non-coordinating anion;

n is an integer in the range of from 0 to 5;

7

$$OR^7_2—M^2=C$$

with OR^7_2 at top, R^4 and R^5 on C, and $N—R^6$ below M^2

Formula III

wherein

M^2 is Mo or W

R^4, R^5 are, independently, hydrogen or a hydrocarbon selected from the group

consisting of C_2-C_{20} alkenyl, C_2-C_{20} alkynyl, C_1-C_{20} alkyl, aryl, C_1-C_{20} carboxylate, C_1-C_{20} alkoxy, C_2-C_{20} alkenyloxy, C2-C_{20} alkynyloxy, aryloxy, C_2-C_{20} alkoxycarbonyl, C_1-C_{20} alkylthio, C_1-C_{20} alkylsulfonyl and C_1-C_{20} alkylsulfinyl;

R^6 and R^7 are independently selected from any unsubstituted or halo-substituted alkyl, aryl, aralkyl groups or silicon-containing analogs thereof.

Catalysts of Formula I are preferred. More preferably, catalysts of Formula I wherein L and L^1 are trialkylphosphines, X and X^1 are chloride ions and M is Ruthenium are preferred.

The amount of catalyst employed in the metathesis reaction will depend upon the nature and activity of the catalyst in question. Typically, the ratio of catalyst to NBR is in the range of from about 0.005 to about 5, preferably in the range of from about 0.025 to about 1 and, more preferably, in the range of from about 0.1 to about 0.5.

The metathesis reaction is carried out in the presence of a co-olefin which is a C_1 to C_{16} linear or branched olefin such as ethylene, isobutene, styrene or 1-hexene. Where the co-olefin is a liquid (such as 1-hexene), the amount of co-olefin employed is in the range of from about 1 to about 50 weight %; preferably in the range of from about 10 to about 30 weight %. Where the co-olefin is a gas (such as ethylene) the amount of co-olefin employed is such that it results in a pressure in the reaction vessel in the range of from about 15 to about 1500 psi, preferably in the range of from about 75 to about 600 psi.

8

The metathesis reaction can be carried out in any suitable solvent which does not inactivate the catalyst or otherwise interfere with the reaction. Preferred solvents include, but are not limited to, dichloromethane, benzene, toluene, tetrahydrofuran,

5 cylcohexane and the like. The most preferred solvent is monochlorobenzene (MCB). In certain cases the co-olefin can itself act as a solvent (for example, 1-hexene), in which case no other solvent is necessary.

The concentration of NBR in the reaction mixture is not critical but, obviously,

10 should be such that the reaction is not hampered if the mixture is too viscous to be stirred efficiently, for example. Preferably, the concentration of NBR is in the range of from about 1 to about 20%, most preferably in the range of from about 6 to about 15%.

The metathesis reaction is carried out at a temperature in the range of from

15 about 20 to about 140°C; preferably in the range of from about 60 to about 120°C.

The reaction time will depend upon a number of factors, including cement concentration, amount of catalyst used and the temperature at which the reaction is performed. The metathesis is complete within the first two hours under typical

20 conditions. The progress of the metathesis reaction may be monitored by standard analytical techniques, for example using GPC or solution viscosity.

Step 2: Hydrogenation

25 Reduction of the product from the metathesis reaction can be effected using standard reduction techniques known in the art. For example, homogeneous hydrogenation catalysts known to those of skill in the art, such as Wilkinson's catalyst {(PPh$_3$)$_3$RhCl} and the like can be used.

30 The hydrogenation may be performed *in situ* i.e. in the same reaction vessel in which the metathesis step is carried out, without the need to first isolate the metathesised product. The hydrogenation catalyst is simply added to the vessel, which is then treated with hydrogen to produce the HNBR.

9

Grubb's catalyst, in the presence of hydrogen, is converted to a dihydride complex $(PR_3)_2RuCl_2H_2$, which is itself an olefin hydrogenation catalyst. Thus, in a one-pot reaction, Grubb's catalyst was used to reduce the molecular weight of NBR in the presence of co-olefin. The reaction mixture was then treated with hydrogen, converting

5 the Grubb's complex to the dihydride species which then hydrogenated the metathesis product to produce the HNBR of the invention. The rate of hydrogenation was lower in this case than in the case where Wilkinson's catalyst was used for the hydrogenation step, but it is clear that such an approach is indeed a viable one.

10 The low Mooney HNBR which forms an object of the invention can be characterized by standard techniques known in the art. For example, the molecular weight distribution of the polymer was determined by gel permeation chromatography (GPC) using a Waters 2690 Separation Module and a Waters 410 Differential Refractometer running Waters Millenium software version 3.05.01. Samples were

15 dissolved in tetrahydrofuran (THF) stabilised with 0.025% BHT. The columns used for the determination were three sequential mixed-B gel column from Polymer Labs. Reference Standards used were polystyrene standards from American Polymer Standards Corp.

20 The Mooney viscosity of the rubber was determined using ASTM test D1646.

For a typical product the Mn is about 27k (compared to 85k for the starting polymer) whilst the Mw is about 54k (compared to 296k for the starting polymer). As expected, the molecular weight distribution falls from about 3.4 for the starting

25 Perbunan NT 3435 T feedstock to about 2.0 for the metathesized product. This is consistent with a more homogeneous range of polymer chain lengths and molecular weights.

A summary of the polymer properties for selected samples is shown in

10

					(ML 1+4 @ 100)
Comparative Therban	98000	320000	945000	3.27	73
Starting NBR	85000	296000	939000	3.50	
Experiment 1	73000	189000	441000	2.59	43
Experiment 2	60000	136000	277000	2.27	28
Experiment 3	31000	59000	98000	1.90	3

Experimental Details

General

5   Tris(triphenylphosphine)Rhodium Chloride (Wilkinson's hydrogenation catalyst), Bis(tricyclohexylphosphine)benzylidene ruthenium dichloride (Grubb's metathesis catalyst), 1-hexene, triphenylphosphine (TPP) and monochlorobenzene (MCB) were purchased from JMI, Alfa, Aldrich Chemicals, Elf Atochem and PPG respectively and used as received.

10

Metathesis

The metathesis reactions were carried out in a Parr high-pressure reactor under the following conditions:

Cement Concentration	6 or 15%
15 Co-Olefin	Ethylene or 1-Hexene
Co-Olefin Concentration	Variable
Agitator Speed	600 rpm
Reactor Temperature	Variable
Catalyst Loading (Grubb's)	Variable
20 Solvent	Monochlorobenzene
Substrate	Perbunan NT 3435 T
	Perbunan NT 3429 T

In a typical lab experiment, 200g of rubber was dissolved in 1133g of MCB (15%
25   solid). The cement was then charged to the reactor and degassed 3 times with C_2H_4 (100 psi) under full agitation. The reactor was heated to desired temperature and 60mL of a monochlorobenzene solution containing Grubb's catalyst was added to the reactor.

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The temperature was maintained constant for the duration of the reaction. A cooling coil connected to a temperature controller and a thermal sensor was used to regulate the temperature. The progress of the reaction was monitored using solution viscosity measurements for the 6% cements. At higher cement concentration, the reaction was
5   assumed to be complete after 18 hours.

Hydrogenation

The hydrogenation reactions were carried out in the same reactor as the metathesis under the following conditions:

10

Cement solid concentration	12%
$H_2(g)$ pressure	1200 psi
Agitator Speed	600 rpm
Reactor Temperature	138°C
Catalyst Loading (Wilkinson's)	0.08 phr
Triphenylphosphine	1 phr
Solvent	Monochlorobenzene

15

In a typical lab experiment, the cement from the metathesis reaction was
20   degassed 3 times with H_2 (100 psi) under full agitation. The temperature of the reactor was raised to 130°C and a 60mL monochlorobenzene solution containing Wilkinson's catalyst and triphenylphosphine was added to the reactor. The temperature was allowed to increase to 138°C and maintained constant for the duration of the reaction. The hydrogenation reaction was monitored by measuring the residual double bond
25   (RDB) level at various intervals using IR spectroscopy.

Alternatively, the Ruthenium metathesis catalyst can be used to hydrogenate the polymer.

12

Claims

1. A hydrogenated nitrile rubber having a molecular weight (M_W) in the range of from about 30,000 to about 250,000 and a polydispersity index of less than about 2.5.

2. A hydrogenated nitrile rubber according to claim 1 wherein the molecular weight (Mw) is in the range of from about 40,000 to about 220,000.

3. A hydrogenated nitrile rubber according to claim 2 wherein the molecular weight (Mw) is in the range of from about 55,000 to about 190,000.

4. A hydrogenated nitrile rubber according to claim 1 wherein the polydispersity index is less than about 2.3.

5. A hydrogenated nitrile rubber according to claim 1 wherein the polydispersity index is less than about 2.1.

6. A hydrogenated nitrile rubber according to claim 1 wherein the rubber has a Mooney viscosity (ML 1+4 100) of less than about 55.

7. A hydrogenated nitrile rubber according to claim 5 wherein the rubber has a Mooney viscosity (ML 1+4 100) of less than about 45.

8. A hydrogenated nitrile rubber according to claim 1 wherein the rubber has a Mooney viscosity (ML 1+4 100) of less than about 35.

9. A hydrogenated nitrile rubber according to claim 1 wherein the rubber has a Mooney viscosity (ML 1+4 100) of less than about 30.

10. A hydrogenated nitrile rubber according to claim 1 wherein the rubber has a Mooney viscosity (ML 1+4 100) of less than about 5.

11. A hydrogenated nitrile rubber having a Mooney viscosity (ML 1+4 100) of less than about 50.

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12. A hydrogenated nitrile rubber according to claim 11 having a Mooney viscosity (ML 1+4 100) of less than about 45.

13. A hydrogenated nitrile rubber according to claim 12 having a Mooney viscosity (ML
5   1+4 100) of less than about 30.

14. A hydrogenated nitrile rubber according to claim 13 having a Mooney viscosity (ML 1+4 100) of less than about 5.

10   15. The use of a hydrogenated nitrile rubber according to claim 1 in the manufacture of a seal. hose. bearing pad, stator. well head seal, valve plate, cable sheathing, wheel, roller or pipe seal.

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